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THEORETICAL CONFIRMATION OF GA-STABILIZED ANTI-FERROMAGNETISM IN PLUTONIUM METAL

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Theoretical confirmation of Ga-stabilized anti-ferromagnetism in plutonium metal

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ABSTRACT

The density-functional-theory model for plutonium metal is shown to be consistent with recent magnetic measurements that suggest anti-ferromagnetism in Pu-Ga alloys at low temperatures. The theoretical model predicts a stabilization of the face-centered-cubic (fcc, δ) form of plutonium in an anti-ferromagnetic configuration when alloyed with gallium. The ordered magnetic phase occurs because Ga removes the mechanical instability that exists for unalloyed δ-Pu. The cause of the Ga-induced stabilization is a combination of a lowering of the band (kinetic) and electrostatic (Coulomb) energies for the cubic relative to the tetragonal phase.

INTRODUCTION

Plutonium metal remains an interesting but complex and controversial material. Particularly, its face-centered cubic (fcc) δ phase has received almost as much attention as the likewise fcc phases in cerium metal (α and γ). In order to stabilize δ-Pu at lower temperatures it is alloyed with a stabilizer, often gallium, and this allows the study of the temperature dependence in a wide temperature range. Recently [1, 2], a piece of the plutonium puzzle was provided by magnetization measurements that was interpreted to show existence of an anti-ferromagnetic phase below a critical temperature of 30 K for the δ-$Pu_{92}Ga_8$ alloy and 40 K for the Pu_3Ga compound. In Figure 1 we redraw the real part of the dynamic susceptibility versus temperature from Arkhipov *et al.* [1] that indicates the critical temperatures.

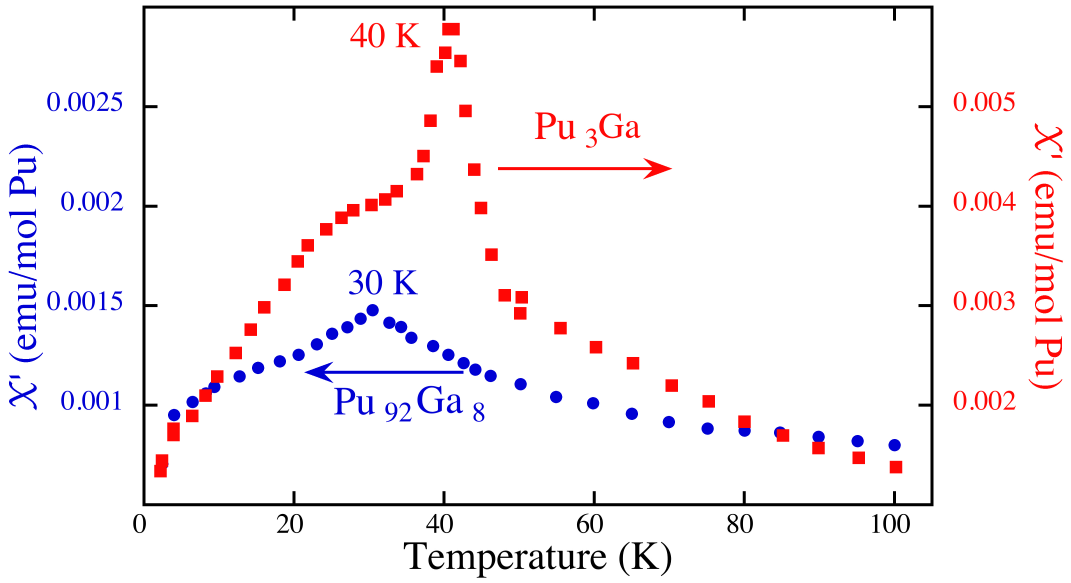

Figure 1. The real part of dynamic susceptibility versus temperature. Taken from Ref. [1].

From a modified Curie-Weiss model the authors [1, 2] were able to determine the critical (Néel) temperatures and thus identify anti-ferromagnetism in the Pu-Ga systems similar to what has been done in the past for other δ-Pu alloys [3].

In this brief report, we investigate whether anti-ferromagnetism in δ-Pu-Ga alloys, at low temperatures, is consistent with the density-functional-theory (DFT) model for Pu metal and Pu-Ga alloys and explore possible causes for such stabilization.

COMPUTATIONAL DETAILS

We are focusing our first-principles modeling on a robust implementation of DFT for which consistent predictions can be made without the uncertainty of model parameters. The full-potential linear muffin-tin orbitals (FPLMTO) method do not compromise on accuracy beyond that necessary for the electron exchange and correlation energy functional, which is chosen to be the generalized gradient approximation (GGA). Although newer varieties of this approximation have been proposed, the GGA remains the preferred choice for actinide metals [4].

Our particular FPLMTO implementation is based on an implementation that has been described in detail [5]. In addition to the choice of GGA, we have found that for actinides no geometrical approximations, "full potential", full relativity including spin-orbit coupling, spin and orbital polarization, and a well converged basis set is often needed for the best accuracy. Specifically, we associate a set of 6*s* and 6*p* semi-core states in addition to the valence states (7*s*, 7*p*, 6*d*, and 5*f*) to two kinetic energy parameters for a so-called double basis set.

The alloy approximation of the δ-Pu-Ga alloy system is accomplished with a 24-atom supercell and 32 k points in the irreducible part of the Brillouin zone are used for the appropriate summations. The supercell approach for the alloy system has recently been validated by calculations applying the coherent potential approximation [6]. 1-3 Ga atoms are chosen to replace Pu atoms in the 24-atom cell, preserving as high crystal symmetry as possible, to model the 4, 8, and 12 at.% δ-Pu-Ga alloy system.

RESULTS

It has been known for some time that DFT predicts formation of spin and orbital moments in plutonium metal [7, 8]. Specifically for δ-Pu, it has been argued that it is paramagnetic with disordered moments [9] and that anti-ferromagnetism is ruled out because of mechanical instability associated with a tetragonal distortion [9, 10]. Adding Ga to δ-Pu, in sufficient but small amounts, however, could remove the mechanical instability and form an anti-ferromagnetic alloy at low temperatures, consistent with the interpretation by Arkhipov *et al.* [1].

In Figure 2 we show the energy dependence on tetragonal distortion for Pu and three Pu-Ga alloys. The upper panel (a) shows results from calculations that do not include spin-orbit interaction while in the lower panel (b) the calculations do. Also, in the lower panel the dashed curve (12 at.% Ga) comes from calculations that include orbital polarization (SO+OP) that has been suggested for δ-Pu [11]. Analyzing this figure, we realize that mechanical stabilization of the fcc (δ) phase occurs for a Ga content close to 8 at.% in the Pu-Ga alloy, but only if spin-orbit interaction is considered. Orbital polarization does not influence the stabilization substantially.

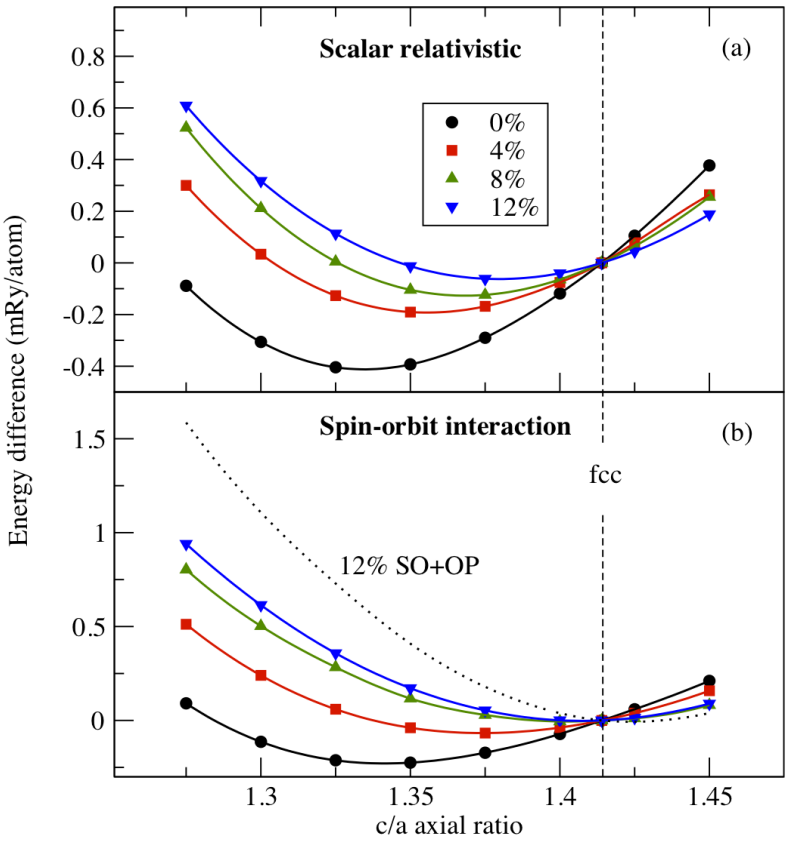

Figure 2. Total energies, relative to that of fcc, as functions of axial *c/a* ratio for unalloyed Pu and three Pu-Ga alloys. The upper panel (a) shows results from a scalar relativistic treatment while for the lower panel (b) spin-orbit interaction is included in the calculations. For comparison, one set of calculations (12 at.% Ga) is performed including orbital polarization (dotted line, no symbols) in panel (b).

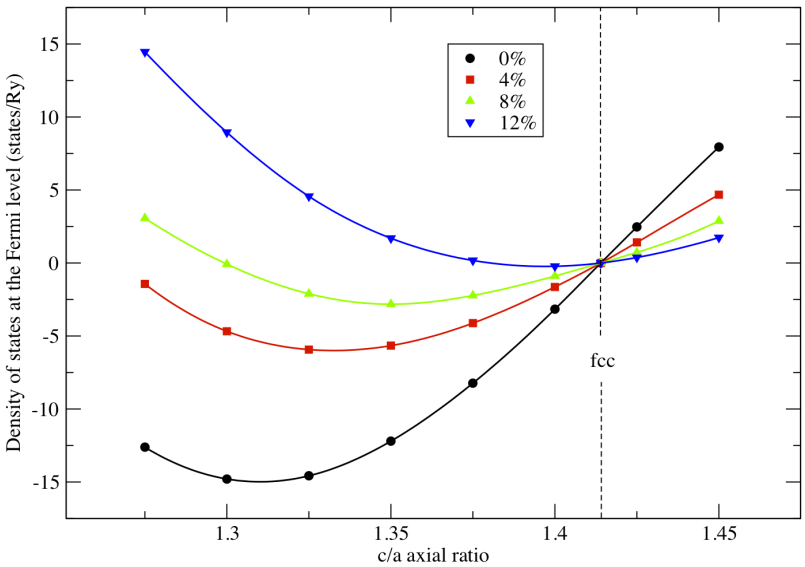

Figure 3. Calculated $D(E_F)$ relative to that of fcc, as functions of *c/a* axial ratio, for unalloyed Pu and three Pu-Ga alloys. The calculations include spin-orbit interaction.

Because crystal-structure distortions in the actinide metals often arise from kinetic (band) energies and the characteristics of the 5*f* band (narrow close to the Fermi energy) [12], balanced by electrostatic energies [13], it is sensible to investigate these potential causes for the stabilization.

In Figure 3 we show the calculated density-of-states at the Fermi level, $D(E_F)$, as a function of tetragonal distortion for Pu and three Pu-Ga alloys. Here we find that the tendency towards destabilization of the fcc phase (low $D(E_F)$ for a *c/a* axial ratio less than 1.414) for unalloyed Pu is removed when adding Ga.

Next, in Figure 4 we plot the electrostatic Madelung energies for Pu and three Pu-Ga alloys [6]. Because the electrostatic energy favors higher symmetry and closer packed crystal structures it is not surprising to find the Madelung-energy minimum close to *c/a* = 1.414 (fcc). For elemental Pu the electrostatic energy is weakly increasing for a tetragonal deformation (*c/a* < 1.414) but, interestingly, this increase is greatly amplified for the Pu-Ga alloys. This then helps to explain the mechanical stabilization of the fcc phase due to alloying [6].

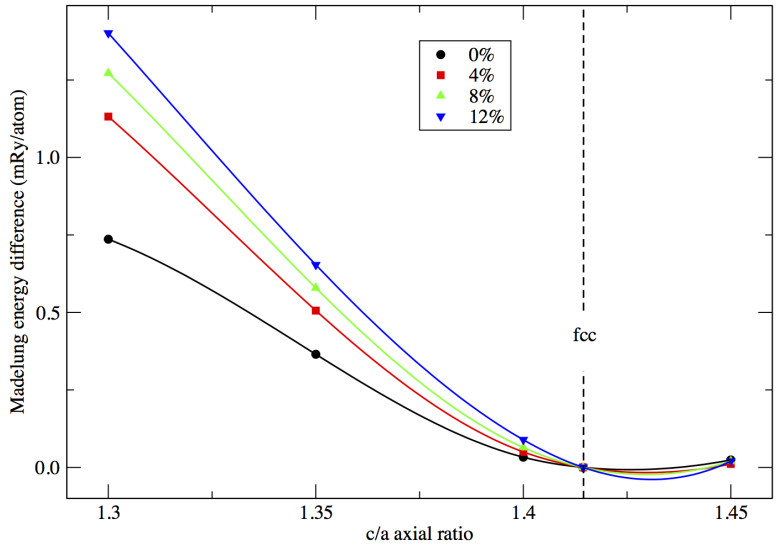

Figure 4. Calculated electrostatic (Madelung) energies, relative to that of fcc, as functions of *c/a* axial ratio for unalloyed Pu and three Pu-Ga alloys. The calculations are scalar relativistic.

In conclusion, the two interactions (kinetic and electrostatic) recognized to help mechanically stabilize the fcc δ phase and sustaining anti-ferromagnetism, are general in nature and not isolated to the Pu-Ga alloy system and we are currently exploring other δ-Pu alloys for which anti-ferromagnetism may exist.

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